Quantum Chemical Approach for Condensed-Phase Thermochemistry (II):

Applications to Formation and Combustion Reactions of

Liquid Organic Molecules

Atsushi Ishikawa^{1,4} and Hiromi Nakai^{1-4, a}

¹ Research Institute for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo

169-8555, Japan

² Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda

University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan

³ CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012,

Japan

⁴ ESICB, Kyoto University, Kyotodaigaku-Katsura, Kyoto 615-8520, Japan

a) To whom correspondence should be addressed. E-mail: nakai@waseda.jp

(Abstract)

The harmonic solvation model (HSM), which was recently developed for evaluating condensed-phase thermodynamics by quantum chemical calculations (*J. Chem. Phys.*, **141**, 174106 (2014)), was applied to formation and combustion reactions of simple organic molecules. The conventional ideal gas model (IGM) considerably overestimated the entropies of the liquid molecules. The HSM could significantly improve this overestimation; mean absolute deviations for the Gibbs energies of the formation and combustion reactions were (49.6, 26.7) for the IGM and (9.7, 5.4) for the HSM in kJ/mol.

Keywords: Quantum chemistry, Condensed phase, Thermodynamics, Free energy, Standard formation reaction, Combustion reaction

1. Introduction

Predicting thermodynamic properties such as enthalpy, entropy, heat capacity, Helmholtz energy, and Gibbs energy at “chemical accuracy” levels, i.e., accuracy at the kJ/mol level, has long been one of the fundamental goals of modern quantum chemistry. Considerable progress has been made in recent years towards the development of methods for highly accurate predictions of thermodynamic properties. Examples of such methods include the Gaussian series (Gn, n = 1, 2, and 3) [1-4], Weizmann model (Wn, n = 1, 2, 3, and 4) [5-6], and the high accuracy extrapolated *ab initio* thermochemistry (HEAT) model [7].

To evaluate enthalpy, entropy, and Gibbs energy, the contributions from nuclear motions should be added to the electronic energy. For gaseous molecules, the separation of nuclear motion into its vibrational, rotational, and translational components is a reasonable approximation both qualitatively as well as quantitatively, as demonstrated in many cases, since intermolecular interactions are negligible [8-10]. Under this assumption, the vibrational, rotational, and translational motions are expressed by the harmonic oscillator, rigid rotor, and particle-in-a-box models, respectively. This treatment, known as the kinetic theory of gases, is often employed under the assumption of the ideal gas model (IGM). Entropy as well as the internal energy can be also readily determined using this treatment, and these values have been also shown to be in good

1 agreement with experimental results [10]. Therefore, the accuracy of the thermodynamic property
2 calculations of gaseous molecules significantly depends on the accuracy of the electronic energy.

3 Electron correlations are crucial to accurately calculate the electronic energies by the wave
4 function theory (WFT), which can systematically approach the exact solution to the Schrödinger
5 equation (at the non-relativistic level) for a given basis set (i.e., the full configuration interaction
6 limit). The electronic energy at the basis set limit is frequently estimated with the extrapolation
7 techniques such as the complete-basis-set (CBS) extrapolation [11-16]. For the electron correlation
8 problem, the coupled cluster with single, double, and non-iterative triple excitations (CCSD(T)) is
9 commonly called a golden-standard method because of its high accuracy. However, higher-level
10 electron correlations (HLC) compared to the CCSD(T) level were required to achieve the accuracy
11 at the kJ/mol level, especially for pathological cases. [5-7] For example, the contributions from
12 HLC to the atomization energies are found to exceed 1 kJ/mol for radicals; in the cases of CN, OF,
13 O₂, and F₂, the HLC contributions are 6.57, 3.15, 2.39, and 2.12 kJ/mol, respectively [7].

14 Furthermore, other contributions such as the diagonal Born-Oppenheimer correction, scalar
15 relativistic and spin-orbit effects are taken into account [17-18]. Among them, the scalar relativistic
16 effect is considered to be the most significant in terms of magnitude, especially for molecules
17 involving third-low or higher elements. The impact of the spin-orbit effect on the calculated

thermodynamic parameters has been shown to be lower than 1 kJ/mol [19].

In the gas phase, all the corrections stated above are meaningful in the evaluation of thermodynamic properties, since the IGM provides vibrational, rotational, and translational energies and entropies with the accuracy at the kJ/mol level. On the other hand, in the condensed phase, the situation is considerably different. Currently, various methods are available for theoretically calculating thermodynamic properties in the condensed phase.

Molecular simulations with explicit inclusion of temperature effects such as molecular dynamics (MD) and Monte Carlo (MC) methods can evaluate the solvation free energies [20]. In these methods, the accuracy of the free energy values strongly depends on the sampling efficiency and the quality of the force field. The issue of sampling efficiency is still under extensive examination by researchers in the MD and MC fields.

One of the widely used quantum chemical methods to treat the condensed phase is the self-consistent reaction field (SCRF) approaches, including the polarizable continuum model (PCM). The SCRF methods incorporate the solvent effect in the solute's Hamiltonian and evaluate the electrostatic term in the solvation free energy [20-22]. In such methods, the total solvation free energy is usually estimated without separating enthalpy and entropy contributions.

The effect of the nuclear motions of the solutes, which is not included explicitly by the SCRF

1 treatment, also contributes to the thermodynamic properties, as in the case of the gas phase.
2 IGM-like procedures are generally adopted even for the calculations of thermodynamic properties
3 in the condensed phase. However, such treatments are not adequate, since the nuclear motions of
4 the solutes are considerably restricted in the condensed phase. In particular, the rotational and
5 translational motions are more restricted in the condensed phase than in the gas phase.

6 We recently proposed a novel quantum chemistry model for condensed-phase molecules,
7 called the “harmonic solvation model” (HSM), where the translational and rotational motions of the
8 solute molecules were treated using harmonic oscillators between the solute molecules and their
9 molecular-shaped cavity walls, effectively treating them as soft vibrational motions within the
10 cavity [23]. The internal energy and entropy in the condensed phase calculated using the HSM
11 significantly improved over the IGM-like treatment. However, the applications of the HSM were
12 limited in the previous work [23]. Thus, the accuracy and usefulness of the HSM were not
13 confirmed.

14 In this Letter, we applied the HSM for calculating the standard enthalpy change (ΔH°) and
15 Gibbs energy change (ΔG°) for the formation and combustion reactions of liquid organic molecules,
16 since experimental values for these properties are abundantly available in the literature [24]. In Sec.
17 2, the theoretical aspects of the IGM and HSM are briefly explained. Section 3 shows the

1 computational details. In Sec. 4 describing the results and discussion, the thermodynamic properties
2 of the formation and combustion reactions of liquid organic molecules are discussed. Finally,
3 concluding remarks are given in Sec. 5.

2. Theoretical Aspects

As stated previously, in the IGM, the motion of gaseous molecules is separated into vibrational, rotational, and translational components, whose energies and entropies may be expressed by

$$E_{\text{vib}} = RT \sum_i^{3N-6} \frac{h\nu_i}{k_B T} \left\{ \frac{1}{2} + \frac{\exp(-h\nu_i/k_B T)}{1 - \exp(-h\nu_i/k_B T)} \right\}, \quad (1)$$

$$E_{\text{rot}} = E_{\text{trans}} = \frac{3}{2} RT, \quad (2)$$

$$S_{\text{vib}} = R \sum_i^{3N-6} \left[\frac{(h\nu_i/k_B T) \exp(-h\nu_i/k_B T)}{1 - \exp(-h\nu_i/k_B T)} - \ln\{1 - \exp(-h\nu_i/k_B T)\} \right], \quad (3)$$

$$S_{\text{rot}} = R \left\{ \frac{1}{2} \ln ABC + \frac{3}{2} \ln T - \ln \sigma + \text{const.} \right\}, \quad (4)$$

$$S_{\text{trans}} = R \left\{ \frac{3}{2} \ln M + \frac{5}{2} \ln T - \ln P + \text{const.} \right\}. \quad (5)$$

In the above equations, h , k_B , and R are the Planck, Boltzmann, and gas constants, respectively. P and T are the pressure and temperature, respectively. The vibrational frequencies $\{\nu_i\}$, mass M , rotational constants $\{A, B, \text{ and } C\}$, and symmetry number σ are system-dependent quantities. By adding these energies and entropies to the electronic energy E_{elec} , the enthalpy H and the Gibbs energy G are readily given by

$$H = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}} + W, \quad (6)$$

$$G = H - TS. \quad (7)$$

The entropy S in Eq. (7) is defined by Eq. (8) and the work W is estimated using the IGM as shown

in Eq. (9).

$$S = S_{\text{elec}} + S_{\text{vib}} + S_{\text{rot}} + S_{\text{trans}} , \quad (8)$$

$$W = PV = RT . \quad (9)$$

Note that the electronic entropy S_{elec} is zero for the standard molecule in the singlet ground state.

In the condensed phase, the rotational and translational motions are restricted by solute-solvent interactions. Consequently, expressions for rotational and translational energies and entropies based on the IGM (Eqs. (2), (4), and (5)) are invalid in the condensed phase. To adequately express these properties, the HSM model treats the rotational and translational motions corresponding to the solute-solvent interactions as harmonic oscillators.

The current HSM treatment is based on the SCRF procedure. The main difference between the IGM and the HSM is in the evaluation of the Hessian matrix and the rotational and translational energies and entropies. In the Hessian matrix evaluations, the solvent cavities are allowed to relax (via the cavity-dependent term in the energy second derivative) in the IGM connected to the SCRF (IGM/SCRF), whereas the cavities are fixed in the HSM connected to the SCRF (HSM/SCRF) and any interactions with the cavities are presumed to be solute-solvent interactions. After the Hessian matrix evaluations, the vibrational, rotational, and translational energies and entropies are evaluated. In the IGM, the rotational and translational modes, which normally correspond to the six lowest

1 modes, are omitted when evaluating the thermal contributions from the vibrational motions. In
2 contrast, in the HSM, all the motions of the solute molecules are treated as harmonic vibrations.
3 Therefore, the rotational and translational energies and entropies were evaluated according to the
4 vibrational formulae [23].

3. Computational Details

In this Letter, we treated eight organic molecules such as formic acid (HCOOH), methanol (CH₃OH), nitromethane (CH₃NO₂), ethanol (C₂H₅OH), acetonitrile (CH₃CN), acetaldehyde (CH₃CHO), acetic acid (CH₃COOH) and benzene (C₆H₆). The standard formation reactions of the molecules in the gas or liquid phase are given as follows:

The standard formation enthalpy ($\Delta_f H^\circ$) and Gibbs energy ($\Delta_f G^\circ$) are defined as the difference in the enthalpy and Gibbs energy between both sides of Eq. (10). Experimental values of -716.7 and -671.3 kJ/mol were used for the sublimation enthalpy and Gibbs energy of solid carbon, respectively [24].

Similarly, the combustion reactions of the liquid molecules are expressed by

Here, experimental values were unnecessary for calculating the thermodynamic parameters. For evaluating the enthalpy and Gibbs energy, the IGM was applied to gaseous molecules, whereas both IGM and HSM were applied to the liquid molecules, for comparison. When $\{n_1, n_2, n_3, n_4\} = \{0, 2, 0, 1\}$, Eq. (10) corresponds to the standard formation of water molecule (H₂O), whereas Eq. (11) to the combustion reaction of hydrogen molecule (H₂).

To deal with the liquid molecules, we adopted the conductor-like PCM (CPCM) procedure, including repulsion and dispersion interaction energies by Floris and Tomasi [25-26]. The cavity radius was based on the van der Waals radius determined by Bondi [27], with a cavity scaling parameter (α) of 1.2, which is often recommended and widely used in PCM calculations [28].

Geometry optimization and frequency analyses were carried out at the second order Møller-Plesset perturbation (MP2) method with Dunning's correlation-consistent polarized valence triple-zeta (cc-pVTZ) basis set [29]. Molecular symmetry was imposed, where available. No scaling factor was applied for the vibrational frequency. The standard state ($T = 298.15$ K, $P = 1$ atm) was assumed in all the thermodynamic property calculations.

For evaluating the electronic energy, the CBS extrapolation was extrapolated for the Hartree-Fock (HF) and correlation energies separately. Using the cardinal number X of the Dunning's correlation consistent basis sets, the CBS HF energy $E_{\text{HF}}^{\text{CBS}}$ was given by the formula proposed by Halkier [30],

$$E_{\text{HF}}^{\text{CBS}} = E_{\text{HF}}^X - A \exp(-BX). \quad (12)$$

We adopted the HF energies of the augmented correlation-consistent polarized core and valence double-, triple-, and quadruple-zeta (aug-cc-pCVXZ ($X = \text{D, T, and Q}$)) basis sets, in order to determine $E_{\text{HF}}^{\text{CBS}}$ as well as the parameters A and B in Eq. (12).

The CBS correlation energy $E_{\text{corr}}^{\text{CBS}}$ was given by the inverse cubic formula by Helgaker [31-32],

$$E_{\text{corr}}^{\text{CBS}} = E_{\text{corr}}^X - CX^{-3}. \quad (13)$$

In order to determine $E_{\text{corr}}^{\text{CBS}}$ as well as the parameter C , we adopted the CCSD(T)/aug-cc-pCVXZ ($X = \text{T and Q}$) levels of theory, in which the correlation effect of all the electrons (core and valence) were included.

The scalar relativistic effect was assumed to be the difference between the energies obtained at the CCSD(T)/aug-cc-pCVTZ-DK level with the second order Douglas-Kroll-Hess (DKH2) Hamiltonian and the non-relativistic CCSD(T)/aug-cc-pCVTZ-DK level.

The HSM procedure was conducted with our original program connected to GAMESS, and frequency analyses with the CPCM were performed with GAMESS2013 [33]. Other calculations such as all the gas-phase calculations, scalar relativistic effect, geometry optimization, and energy evaluation in the condensed phase were performed using Gaussian09 Revision C [34].

4. Results and Discussion

4.1. Standard Formation Reactions of Gas- and Liquid-Phase Molecules

This subsection describes the standard formation reactions of the eight organic molecules in the gas/liquid phase given in Eq. (10). Table I summarizes $\Delta_f H^\circ$, $\Delta_f G^\circ$, and third-law entropy S° . As expected, the gas-phase values agree well with experimental values. The largest deviation of $\Delta_f H^\circ$ (+5.8 kJ/mol) from the experimental value was observed for nitromethane molecules. The values of $\Delta_f G^\circ$ also agreed well with experimental values, and in this case, the largest deviation was observed for benzene (−17.8 kJ/mol). The mean absolute deviations (MAD) of $\Delta_f H^\circ$ and $\Delta_f G^\circ$ from the experimental results [24] were 1.8 and 4.1 kJ/mol, respectively. Similarly, the gas-phase entropy $S^\circ(\text{g})$ was correctly evaluated. The MAD of $S^\circ(\text{g})$ was 4.9 J/mol/K, whereas the largest deviation for $S^\circ(\text{g})$ was observed for acetaldehyde, which was −12.6 J/mol/K. Therefore, it may be concluded that the current computations in the IGM were accurate in the kJ/mol order for gaseous molecules.

The scalar relativistic effect on the formation enthalpy is 1 to 5 kJ/mol, the smallest in the water molecule (0.8 kJ/mol) and the largest in the benzene molecule (4.2 kJ/mol); see Table S1 in Supplementary Material.

Next, let us discuss the results of the liquid-phase calculations in the IGM. The MAD of $\Delta_f H^\circ$ is 10.9 kJ/mol and the largest deviation is −23.8 kJ/mol for acetaldehyde. In contrast, $\Delta_f G^\circ$

1 calculated using IGM were significantly different from the experimental values with a MAD of 49.6
2 kJ/mol. Significant deviations in the $\Delta_f G^\circ$ values predicted using IGM stemmed from the incorrect
3 evaluations of the liquid-phase entropy $S^\circ(\ell)$, since the IGM considerably overestimated $S^\circ(\ell)$. For
4 many molecules, $S^\circ(\ell)$ and $S^\circ(g)$ possessed similar values, as seen in the last column in Table 1.
5 Since the nuclear motions in the liquid phase should be more limited than those in the gas phase,
6 $S^\circ(\ell)$ calculated by the IGM was incorrect.

7 Unlike the IGM, the HSM treated the entropy component in the liquid phase differently than
8 in the gas phase. Consequently, $S^\circ(\ell)$ was considerably smaller than $S^\circ(g)$. The entropy difference
9 between the gas and liquid phases ($S^\circ(g) - S^\circ(\ell)$) was approximately zero or slightly negative in the
10 IGM for all the molecules in Table 1: that is, -4.3 J/mol/K on average. In contrast, $S^\circ(g) - S^\circ(\ell)$
11 calculated using the HSM averaged out at 147.0 J/mol/K, which was close to the experimental
12 values: i.e., 110.1 J/mol/K on average. As expected from the improvement in $S^\circ(\ell)$, accurate
13 prediction was observed in the $\Delta_f G^\circ$ calculated using the HSM. The MAD for $\Delta_f G^\circ$ in the IGM and
14 HSM are 49.6 and 9.7 kJ/mol, respectively.

15 Strictly speaking, the current HSM predictions slightly underestimated the experimental
16 liquid-phase entropies $S^\circ(\ell)$ for all the molecules. The HSM approximates the translational and
17 rotational motions of the solute molecule using harmonic oscillators. Inclusion of the anharmonicity

1 effect, which basically reduces the vibrational frequencies, is expected to improve the
2 underestimation of the liquid-phase entropy.

3 Figure 1 shows correlations between the experimental and computed liquid-phase values for
4 (a) $\Delta_f H^\circ$, (b) $\Delta_f G^\circ$, and (c) entropy contributions to the Gibbs energy ($T\Delta_f S^\circ$, where $T = 298.15$ K).
5 As shown in Fig. 1(a), the $\Delta_f H^\circ$ values calculated using IGM and HSM showed reasonable
6 agreements with the experimental values. However, the $\Delta_f G^\circ$ and $T\Delta_f S^\circ$ values in the IGM were
7 unreasonably large. The HSM considerably improved the predictions.

4.2. Combustion Reaction of Organic Liquid-Phase Molecules

This subsection considers the combustion reactions of the eight organic molecules in the liquid phase given in Eq. (11). In Table 2, the enthalpy ($\Delta_c H^\circ$) and the Gibbs energy ($\Delta_c G^\circ$) of combustion calculated using the IGM and HSM are summarized, along with the corresponding experimental values. Entropy contributions to the Gibbs energy ($T\Delta_c S^\circ$) are also shown.

As expected from the previous results for the formation reactions, predictions of $\Delta_c G^\circ$ were considerably improved using the HSM. The MAD of $\Delta_c H^\circ$, $\Delta_c G^\circ$ and $T\Delta_c S^\circ$ calculated using the IGM are 12.9, 26.7 and 36.2 kJ/mol, respectively, whereas the corresponding values for the HSM are 9.5, 5.4, and 5.4 kJ/mol, respectively.

Careful observations of the IGM results led to the following conclusion; the accuracy of the Gibbs energy predicted in the IGM was strongly related to the stoichiometric coefficients of the liquid molecules. For example, the combustion of formic acid is written as shown in Eq. (14).

In this case, both sides of the reaction have the same number of liquid molecules. Therefore, the errors in the evaluation of the entropy term were nullified. Consequently, the IGM predicted $\Delta_c G^\circ$ accurately for the case of formic acid (Table 2). In contrast, the combustion of methanol has different numbers of liquid molecules on the two sides of the reaction:

2 Therefore, there was a significant error in the entropy prediction.

3 Figure 2 schematically illustrates the differences between the theoretical and experimental
4 values for $\Delta_c G^\circ$ and $T_c \Delta S^\circ$ in Table 2 with respect to the difference n in the stoichiometric
5 coefficients of the liquid molecules on the two sides of the reactions. Clearly, the IGM exhibited a
6 larger error as n increased. In contrast, the accuracy of $T_c \Delta S^\circ$ predictions was improved with the
7 HSM, yielding accurate $\Delta_c G^\circ$ values even when n was large.

8 Our analysis on $\Delta_c G^\circ$ with respect to the stoichiometric coefficients of the liquid molecules
9 highlights the advantages of the HSM over the IGM. Accuracy in the prediction of thermodynamic
10 quantities for the combustion reactions strongly depends on the stoichiometric coefficients of the
11 liquid molecules when IGM is employed. In contrast, such dependence is not observed when the
12 HSM is employed because accurate entropy values for liquid molecules are obtained. From this
13 viewpoint, the HSM accurately predicts the thermodynamic quantities for liquid molecules.

5. Concluding Remarks

In this Letter, the HSM was applied for calculating the enthalpy, entropy, and Gibbs energy for the formation and combustion reactions of simple molecules, which are in the liquid phase under the standard state conditions. The HSM enabled the accurate evaluation of liquid-phase entropy by treating the translational and rotational motions as soft vibrations. Adequate evaluations of liquid-phase entropies improved the accuracy in the Gibbs energy predictions in the liquid phase. Significant improvements in $\Delta_f G^\circ$ were observed using the HSM method, as evidenced by the MAD for $\Delta_f G^\circ$: i.e., 49.6 and 9.7 kJ/mol for the IGM and HSM, respectively. The difference between the gas- and liquid-phase entropies ($S^\circ(\text{g}) - S^\circ(\text{l})$) calculated using IGM was estimated to be extremely small, because the IGM used the same formulae in the gas and liquid phases. On the other hand, the HSM yielded reasonable values comparing with the experimental values. Note that the entropy difference $S^\circ(\text{g}) - S^\circ(\text{l})$ is an essential property to cause various phenomena related to the gas and liquid phases properties, e.g., boiling of liquid and condensation of gas.

The enthalpy and Gibbs energy changes for the combustion reactions of the liquid organic molecules were also calculated by the HSM method. The MAD for the combustion Gibbs energy ($\Delta_c G^\circ$) was 26.7 and 5.4 kJ/mol for IGM and HSM, respectively. Interestingly, the accuracy in the calculated Gibbs energies was strongly dependent on the stoichiometric coefficients of the liquid

1 molecules. When the number of liquid-phase molecules on both sides of the combustion reaction
2 was the same, the errors originating in the overestimation of the entropy terms were nullified.
3 Consequently, both IGM and HSM yielded moderately accurate Gibbs energy values. However,
4 when the numbers of liquid molecules on the two sides of the reactions were different, the errors
5 could not cancel out. Therefore, the combustion Gibbs energies predicted by the IGM involved
6 systematic errors. In contrast, since the entropy predictions using the HSM were constantly accurate
7 for liquid molecules.

8 Despite the systematic errors by the IGM, many theoretical studies that reported the
9 thermodynamics of the reactions used the IGM-like treatment even for liquid molecules. One of the
10 reasons might be that the standard quantum chemical programs adopt this treatment. Namely, the
11 users of the program had no other choices. The current work has highlighted the advantages of the
12 HSM for evaluating fundamental thermodynamic parameters such as $\Delta_f H^\circ$, $\Delta_f G^\circ$, $\Delta_c H^\circ$, and $\Delta_c G^\circ$
13 for liquid molecules. Therefore, we strongly recommend to use the HSM, as an alternative to the
14 IGM, for investigating condensed-phase thermodynamics using quantum chemistry.

Acknowledgements

Some of the present calculations were performed at the Research Center for Computational Science (RCCS), the Okazaki Research Facilities, and the National Institutes of Natural Sciences (NINS). This study was supported in part by the Core Research for Evolutional Science and Technology (CREST) program from the Japan Science and Technology (JST) Agency, the Strategic Programs for Innovative Research (SPIRE) and the Computational Materials Science Initiative (CMSI) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

- [1] L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, J. A. Pople, J. Chem. Phys., 93 (1990) 2537.
- [2] L. A. Curtiss, K. Raghavachari, G. W. Trucks, J. A. Pople, J. Chem. Phys., 94 (1991) 7221.
- [3] L. A. Curtiss, P. C. Redfern, B. J. Smith, L. Radom, J. Chem. Phys., 104 (1996) 5148.
- [4] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, J. A. Pople, J. Chem. Phys., 109 (1998) 7764.
- [5] E. C. Barnes, G. A. Petersson, J. A. Montgomery, Jr., M. J. Frisch, J. M. L. Martin, J. Chem. Theory Comput., 5 (2009) 2687.
- [6] J. M. L. Martin, G. de Oliveira, J. Chem. Phys., 111 (1999) 1843.
- [7] A. Tajti, P. G. Szalay, A. G. Csaszar, M. Kallay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vazquez, J. F. Stanton, J. Chem. Phys., 121 (2004) 11599.
- [8] N. O. Smith, Elementary Statistical Physics, Plenum Press, New York, 1982.
- [9] W. Greiner, L. Neise, H. Stöcker, Thermodynamics and Statistical Mechanics, Springer-Verlag, New York, 1995.
- [10] D. A. McQuarrie, J. D. Simon, Physical Chemistry: A Molecular Approach, University Science Books, VA, 1997.
- [11] G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Allaham, W. A. Shirley, J. Mantzaris, J. Chem. Phys., 89 (1988) 2193.
- [12] G. A. Petersson, M. A. Allaham, J. Chem. Phys., 94 (1991) 6081.
- [13] G. A. Petersson, T. G. Tensfeldt, J. A. Montgomery, J. Chem. Phys., 94 (1991) 6091.
- [14] J. A. Montgomery, J. W. Ochterski, G. A. Petersson, J. Chem. Phys., 101 (1994) 5900.
- [15] J. W. Ochterski, G. A. Petersson, J. A. Montgomery, J. Chem. Phys., 104 (1996) 2598.
- [16] J. A. Montgomery, M. J. Frisch, J. W. Ochterski, G. A. Petersson, J. Chem. Phys., 110 (1999) 2822.
- [17] D. Feller, K. A. Peterson, D. A. Dixon, J. Phys. Chem. A, 115 (2011) 1440.
- [18] A. G. Csaszar, W. D. Allen, H. F. Schaefer, J. Chem. Phys., 108 (1998) 9751.
- [19] D. Feller, K. A. Peterson, J. Chem. Phys., 126 (2007).
- [20] P. Kollman, Chem. Rev., 93 (1993) 2395.
- [21] W. L. Jorgensen, Acc. Chem. Res., 22 (1989) 184.
- [22] T. Simonson, G. Archontis, M. Karplus, Acc. Chem. Res., 35 (2002) 430.
- [23] H. Nakai, A. Ishikawa, J. Chem. Phys., 141 (2014).
- [24] CRC Handbook of Chemistry and Physics, 87th ed., CRC Press, Boca Raton, FL., 2006.
- [25] F. Floris, J. Tomasi, J. Comput. Chem., 10 (1989) 616.
- [26] F. M. Floris, J. Tomasi, J. L. P. Ahuir, J. Comput. Chem., 12 (1991) 784.
- [27] A. Bondi, J. Phys. Chem., 68 (1964) 441.
- [28] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev., 105 (2005) 2999.
- [29] T. H. Dunning, J. Chem. Phys., 90 (1989) 1007.
- [30] A. Halkier, T. Helgaker, P. Jorgensen, W. Klopper, J. Olsen, Chem. Phys. Lett., 302 (1999) 437.

- [31] A. Halkier, T. Helgaker, P. Jorgensen, W. Klopper, H. Koch, J. Olsen, A. K. Wilson, *Chem. Phys. Lett.*, 286 (1998) 243.
- [32] T. Helgaker, W. Klopper, H. Koch, J. Noga, *J. Chem. Phys.*, 106 (1997) 9639.
- [33] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.*, 14 (1993) 1347.
- [34] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision C.01*, , in, Gaussian Inc., Wallingford, CT, 2009.

Tables and Figures

Table 1. Standard enthalpy ($\Delta_f H^\circ$) and Gibbs energy ($\Delta_f G^\circ$) of formation, calculated by IGM and HSM methods. Gas- and liquid-phase entropies (S°) are also shown. Errors from the experimental results are shown in parentheses. CCSD(T)/CBS//MP2/cc-pVTZ were used for electronic energy calculations.

Entry	Molecule	Model	Gas phase						Liquid phase						$S^\circ(\text{g}) - S^\circ(\text{l})$ (J/mol/K)	
			$\Delta_f H^\circ$ (kJ/mol)		$\Delta_f G^\circ$ (kJ/mol)		$S^\circ(\text{g})$ (J/mol/K)		$\Delta_f H^\circ$ (kJ/mol)		$\Delta_f G^\circ$ (kJ/mol)		$S^\circ(\text{l})$ (J/mol/K)			
#1	Water (H ₂ O)	IGM	-244.6	(-2.8)	-231.5	(-2.9)	188.4	(-0.4)	-283.3	(+2.5)	-270.2	(-33.1)	188.5	(+118.5)	-0.1	(-118.9)
		HSM	—	—	—	—	—	—	-287.0	(-1.2)	-236.0	(+1.1)	61.4	(-8.6)	127.0	(+8.2)
		Exptl.	-241.8	—	-228.6	—	188.8	—	-285.8	—	-237.1	—	70.0	—	118.8	—
#2	Formic acid (HCOOH)	IGM	-380.6	(-1.9)	-355.7	—	248.0	—	-432.6	(-7.6)	-407.7	(-46.3)	248.0	(+119.0)	0.0	—
		HSM	—	—	—	—	—	—	-437.1	(-12.1)	-366.3	(-4.9)	94.1	(-34.9)	153.9	—
		Exptl.	-378.7	—	—	—	—	—	-425.0	—	-361.4	—	129.0	—	—	—
#3	Methanol (CH ₃ OH)	IGM	-202.1	(-1.1)	-166.0	(-3.7)	237.8	(-2.1)	-242.5	(-3.3)	-206.4	(-39.8)	238.2	(+111.4)	-0.4	(-113.5)
		HSM	—	—	—	—	—	—	-246.7	(-7.5)	-168.6	(-2.0)	97.0	(-29.8)	140.8	(+27.7)
		Exptl.	-201.0	—	-162.3	—	239.9	—	-239.2	—	-166.6	—	126.8	—	113.1	—
#4	Nitromethane (CH ₃ NO ₂)	IGM	-75.0	(+5.8)	-14.9	—	290.4	(-7.5)	-130.9	(-18.3)	-73.3	(-58.9)	299.7	(+127.9)	-9.3	(-120.4)
		HSM	—	—	—	—	—	—	-137.6	(-25.0)	-26.0	(-11.6)	118.0	(-53.8)	172.4	(+61.3)
		Exptl.	-80.8	—	—	—	282.9	—	-112.6	—	-14.4	—	171.8	—	111.1	—
#5	Ethanol (C ₂ H ₅ OH)	IGM	-235.7	(-0.9)	-171.4	(-3.5)	269.5	(-12.1)	-284.8	(-7.2)	-220.8	(-46.0)	270.6	(+109.9)	-1.1	(-122.0)
		HSM	—	—	—	—	—	—	-289.2	(-11.6)	-173.7	(+1.1)	98.2	(-62.5)	171.3	(+50.4)
		Exptl.	-234.8	—	-167.9	—	281.6	—	-277.6	—	-174.8	—	160.7	—	120.9	—
#6	Acetonitrile (CH ₃ CN)	IGM	74.9	(+0.9)	87.1	(-4.8)	243.0	(-0.4)	28.2	(-12.4)	37.8	(-48.7)	251.5	(+101.9)	-8.5	(-102.3)
		HSM	—	—	—	—	—	—	23.5	(-17.1)	76.9	(-9.6)	104.7	(-44.9)	138.3	(+44.5)
		Exptl.	74.0	—	91.9	—	243.4	—	40.6	—	86.5	—	149.6	—	92.8	—
#7	Acetaldehyde (CH ₃ CHO)	IGM	-163.5	(+2.7)	-132.4	(+0.6)	251.2	(-12.6)	-216.0	(-23.8)	-187.7	(-60.1)	260.4	(+100.2)	-9.2	(-112.8)
		HSM	—	—	—	—	—	—	-220.2	(-28.0)	-148.9	(-21.3)	116.3	(-43.9)	134.9	(+31.3)
		Exptl.	-166.2	—	-133.0	—	263.8	—	-192.2	—	-127.6	—	160.2	—	103.6	—
#8	Acetic acid (CH ₃ COOH)	IGM	-432.8	(-0.6)	-381.8	(-7.6)	287.0	(+3.5)	-490.8	(-6.5)	-438.8	(-48.9)	283.6	(+123.8)	3.4	(-120.3)
		HSM	—	—	—	—	—	—	-497.9	(-13.6)	-395.1	(-5.2)	112.9	(-46.9)	174.1	(+50.4)
		Exptl.	-432.2	—	-374.2	—	283.5	—	-484.3	—	-389.9	—	159.8	—	123.7	—
#9	Benzene (C ₆ H ₆)	IGM	82.1	(-0.8)	111.9	(-17.8)	268.6	(-0.6)	32.6	(-16.5)	59.7	(-64.8)	277.7	(+104.3)	-9.1	(-104.9)
		HSM	—	—	—	—	—	—	28.9	(-20.2)	93.7	(-30.8)	151.6	(-21.8)	117.0	(+21.2)
		Exptl.	82.9	—	129.7	—	269.2	—	49.1	—	124.5	—	173.4	—	95.8	—
	MAD	IGM	—	(1.9)	—	(4.5)	—	(4.9)	—	(10.9)	—	(49.6)	—	(113.0)	—	(101.7)
		HSM	—	—	—	—	—	—	—	(15.1)	—	(9.7)	—	(38.6)	—	(32.8)

Table 2. Combustion enthalpy ($\Delta_c H^\circ$) and Gibbs energy ($\Delta_c G^\circ$) for liquid organic molecules, calculated by the IGM and HSM methods. Entropy contributions to the combustion Gibbs energy ($T\Delta_c S^\circ$) are also shown. Errors from the experimental results are shown in parentheses.

		$\Delta_c H^\circ$ (kJ/mol)		$\Delta_c G^\circ$ (kJ/mol)		$T\Delta_c S^\circ$ (kJ/mol)	
Methanol (CH ₃ OH)	IGM	-718.9	(+7.2)	-732.3	(-30.3)	+13.4	(+37.5)
	HSM	-722.1	(+4.0)	-701.7	(+0.3)	-20.3	(+3.8)
	Exptl.	-726.1		-702.0		-24.1	
Ethanol (C ₂ H ₅ OH)	IGM	-1355.2	(+11.6)	-1387.5	(-62.2)	+32.3	(+73.8)
	HSM	-1361.4	(+5.4)	-1326.9	(-1.6)	-34.5	(+7.0)
	Exptl.	-1366.8		-1325.3		-41.5	
Formic acid (HCOOH)	IGM	-246.5	(+8.1)	-261.9	(+8.2)	+15.4	(-0.1)
	HSM	-245.7	(+8.9)	-269.1	(+1.0)	+23.4	(+7.9)
	Exptl.	-254.6		-270.1		+15.5	
Acetic acid (CH ₃ COOH)	IGM	-866.3	(+7.9)	-899.3	(-26.2)	+33.0	(+34.1)
	HSM	-874.4	(-0.2)	-870.8	(+2.3)	-3.6	(-2.5)
	Exptl.	-874.2		-873.1		-1.1	
Acetaldehyde (CH ₃ CHO)	IGM	-1140.6	(+26.3)	-1149.9	(-14.5)	+9.4	(+40.9)
	HSM	-1143.8	(+23.1)	-1120.3	(+15.1)	-23.5	(+8.0)
	Exptl.	-1166.9		-1135.4		-31.5	
Nitromethane (CH ₃ NO ₂)	IGM	-688.8	(+20.4)	-730.4	(+5.3)	+41.5	(+15.0)
	HSM	-687.7	(+21.5)	-726.4	(+9.3)	+38.7	(+12.2)
	Exptl.	-709.2		-735.7		+26.5	
Acetonitrile (CH ₃ CN)	IGM	-1242.6	(+4.6)	-1239.8	(-8.8)	-2.8	(+13.4)
	HSM	-1244.0	(+3.2)	-1228.1	(+2.9)	-15.9	(+0.3)
	Exptl.	-1247.2		-1231.0		-16.2	
Benzene (C ₆ H ₆)	IGM	-3250.8	(+16.8)	-3260.4	(-58.2)	+9.6	(+75.0)
	HSM	-3258.3	(+9.3)	-3191.8	(+10.4)	-66.5	(-1.1)
	Exptl.	-3267.6		-3202.2		-65.4	
MAD	IGM		(12.9)		(26.7)		(36.2)
	HSM		(9.5)		(5.4)		(5.4)

Figure 1. Correlations between experimental and theoretical (IGM and HSM) values for (a) the standard formation enthalpy, (b) Gibbs energy, and (c) the entropy

contributions to the Gibbs energy, shown in Table 1. Numbers in the figures corresponds to the entries in Table 1.

Figure 2. Errors in the theoretical values calculated by IGM and HSM when compared with experimental results for

(a) combustion Gibbs energy and (b) entropy contribution. n is the difference in the stoichiometric coefficients for the

liquid molecules between the two sides of the combustion reactions.

Graphical Abstract

Harmonic Solvation Model